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(54) Self-thickened acidic cleaning compositions

(57) The present invention relates to liquid acidic thickened compositions having a viscosity of at least 10 m Pa s, when measured with a Carri-med rheometer at 5 N/m² at 20°C, and a pH below 4, said composition comprising a thickening system comprising a zwitterionic surfactant and an anionic surfactant at a weight ratio of said zwitterionic surfactant to said anionic surfactant of at least 2:1, and from 0.1% to 70% by weight of the total composition of an acid. Said compositions deliver excellent limescale removal performance as well as outstanding greasy soap scum cleaning on hard-surfaces. The compositions are suitable for the cleaning of non-horizontal and horizontal surfaces.

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Descripti n

Technical Field

5 The present invention relates to liquid acidic self-thickened compositions designed for optimum performance in removing limescale.

Background of the Invention

10 Tap water contains a certain amount of solubilized ions which upon water evaporation eventually deposit as salts such as calcium carbonate on surfaces which are often in contact with water, resulting in an unaesthetic aspect of the surfaces. This limescale formation and deposition phenomenon is even more acute in places where water is particularly hard.

It is well-known in the art that limescale deposits can be chemically removed with acidic solutions, and a great variety of acidic cleaning compositions have been described for this purpose.

15 However, the state of the art liquid acidic limescale removal compositions do not perform equally well on all limescale-containing stains, particularly on limescale-containing stains which can be found in bathrooms or in kitchens, i.e., on stains containing mineral deposits like calcium and/or magnesium carbonate but also high amount of organic deposits such as greasy soap scum, i.e. soap scum and other greasy soils typically occurring in daily usage of bathrooms, e.g. 20 body soils, and/or greasy soils typically occurring in daily usage of kitchens. Indeed, the presence of such greasy soap scum is detrimental to the limescale removal performance of conventional acidic compositions.

Thus, there is a constant need for the development of limescale removal compositions with better performance in several respects including improved greasy soap scum cleaning performance and excellent limescale removal performance.

25 Furthermore, kitchen and/or bathrooms limescale-containing stains are mainly found in such places as sinks and bathtubs, i.e. vertical or inclined surfaces. Therefore, it is desirable to give some viscosity to compositions for removing limescale so as to prevent the compositions from running down such surfaces. Indeed, thickened compositions cling on vertical or inclined surfaces, thus they have more time to act on such surfaces before they run down such surfaces. It is however undesirable to use thickener compounds in such compositions, as the essential ingredients to provide viscosity. 30 Indeed, thickener compounds may significantly raise the formula costs, while providing only one main benefit, which is thickening. Furthermore, they do not participate to the actual cleaning of the surface and therefore represent "inert" materials.

Although viscous compositions are desired, there are some drawbacks associated with product viscosity. And a main drawback is that viscous compositions are typically difficult to rinse away because they have a good cling onto surfaces. 35 Thus, viscosity and ease of rinsing are somewhat conflicting requirements, but both are desirable in a single composition for removing limescale deposits from hard surfaces.

It is therefore desirable to provide thickened limescale removal compositions which are viscous by means of a self-thickening system, and which are nevertheless easy to rinse away.

40 Many self thickening surfactant systems known in the art may provide the requisite viscosity characteristics. However, most of the self-thickening surfactant systems known in the art, whilst allowing to effectively increase the viscosity of a given liquid composition, do have some disadvantages in use. Indeed, thickening surfactants systems like combination of different nonionic surfactants (nonyl phenol ethoxylates) have the disadvantage that they require to be used at high levels to achieve satisfactory viscosity, thus making their use expensive. Also some self-thickening systems may not be stable at the very acidic conditions of the limescale removal compositions of the present invention because the 45 surfactants themselves can be hydrolysed.

It is thus another object of the present invention to formulate liquid self-thickened limescale removal compositions having improved thickening properties at a low total thickening surfactant level.

50 More particularly, it is an object of the present invention to provide a self-thickened liquid composition for the removal of limescale-containing stains, typically found in a kitchen or in a bathroom, which delivers effective limescale removal performance as well as excellent greasy soap scum cleaning performance.

It has now been found, that by combining a zwitterionic surfactant preferably a sulfobetaine surfactant, as a primary surfactant, with an anionic surfactant, preferably a primary or secondary C₆-C₂₀ alkyl sulphonate and/or a primary or secondary C₆-C₂₀ alkyl aryl sulphonates, at a weight ratio of the zwitterionic surfactant to the anionic surfactant of more than 2:1, in an acidic composition comprising an acid, improved thickening properties are delivered to said composition 55 while being nevertheless easy to rinse away. Indeed, the present invention allows to use low level of total thickening surfactants to achieve a given viscosity. In other words, to obtain a desired thickening effect for a given liquid acidic composition comprising at least an acid, a lower total level of thickening surfactants (i.e., zwitterionic surfactants and anionic surfactants) is sufficient in the present invention, as compared to the level of other self-thickening systems like for exam-

ple nonionic surfactant systems required to get the same thickening effect.

Furthermore, it has unexpectedly been found that not only effective viscosity is provided to the acidic compositions of the present invention comprising a zwitterionic surfactant and an anionic surfactant in the appropriate ratios as described herein but these compositions also deliver improved limescale removal performance and improved greasy soap scum cleaning performance. More particularly, it has now been found that the presence of the zwitterionic surfactants, especially sulfobetaine surfactants, as the primary surfactant in the acidic limescale removal compositions of the present invention provides improved limescale removal performance and inhibit soap scum deposition on a surface first treated with such a composition, ensuring thereby long lasting soap scum cleaning to said surface.

The acidic liquid thickened compositions according to the present invention exhibit excellent chemical and physical stability.

A further advantage of the present invention is that the liquid thickened compositions herein are translucent, as opposed to clouded, and thus well accepted from a consumer view point. Also, the present invention allows to formulate compositions that are Newtonian. By "Newtonian", it is meant herein a composition which has the same viscosity whichever applied shear stress, as opposed to "pseudoplastic" compositions, i.e. thickened compositions whose viscosity depends on the shear stress applied. Thus, a benefit of the present invention is that this thickening system leads to newtonian compositions whose effectiveness in removing limescale from hard surfaces does not depend on whether the surface is inclined or horizontal. Indeed, excellent limescale removing performance is delivered with the compositions of the present invention on both inclined/vertical or horizontal surfaces. In contrast, thickened compositions with a pseudoplastic behaviour having the same viscosity of a newtonian composition when applied on an inclined surface, i.e., at a high shear rate typically of 5 N/m^2 , would have a very high viscosity at lower shear rates, i.e., when this pseudoplastic composition is applied on horizontal surfaces, and thus a greatly depressed ability of removing limescale on such a horizontal surface. Indeed, at such very high viscosities the release of CO_2 is reduced, thus resulting in a slower reaction between the acids present in the acidic compositions and limescale deposits.

Yet another benefit of the present invention is that this thickening system according to the present invention leads to excellent spreading. Indeed, the compositions of the present invention have a much lower yield value, i.e. the minimum shear stress required to have the composition start flowing, than pseudoplastic compositions. This means that the compositions of the present invention spread over the surface to be treated more uniformly, thus requiring less product per unit area to be treated and resulting thereby in a higher product effectiveness/quantity ratio.

Another advantage of the present invention is that the preferred acidic compositions of the present invention comprising maleic acid together with a second acid typically sulfamic acid are effective limescale removal compositions while being safe to various surfaces including metal surfaces such as aluminium, chromed steel or stainless steel as well as synthetic materials and to the user skin.

Background art

WO95/33024 discloses an aqueous viscous composition ($\text{pH} = 0.5-7$) comprising an amine oxide or amine and a secondary or primary monobranched alkyl sulphate or sulphonate in excess to said amine or amine oxide, a hydrotrope and an organic acid. No zwitterionic surfactants are disclosed.

GB 2071 688 discloses liquid acidic compositions comprising an inorganic acid and as a thickening agent a mixture of an amine or amine oxide with a cationic or nonionic surfactant. No anionic surfactants and no zwitterionic surfactants are disclosed.

EP-A-265 979 discloses acidic thickened aqueous cleaning compositions comprising a disinfecting and/or oxidising agent, an organic anionic sulphonate selected from the group consisting of xylene sulphonate, cumene sulphonate and toluene sulphonate, and a surfactant selected from the group of (1) quaternary ammonium compounds wherein at least one of the hydrocarbon groups linked to the nitrogen is a linear or branched alkyl group containing at least 12 carbon atoms and of (2) tertiary amine oxides wherein at least one of the hydrocarbon groups linked to the nitrogen is a linear or branched alkyl group containing at least 16 carbon atoms. In contrast, the present invention uses zwitterionic surfactants like betaine and/or sulfobetaine surfactants together with anionic surfactants in a weight ratio of the zwitterionic surfactant to the anionic surfactant of at least 2:1, as the thickening system.

EP-A-188 025 discloses aqueous stable thickened low-pH bleaching compositions comprising an inorganic peroxy compound, a strong acid and a thickening surfactant. The compositions are said to have a viscosity of 10 to 250 mPa s. The thickening surfactant is selected from (1) amine oxides wherein at least one of the hydrocarbon groups linked to the nitrogen is a linear or branched alkyl group of C6 to C18 carbon atoms, preferably C12 to C18, (2) amines and (3) quaternary ammonium salts wherein at least one of the hydrocarbon groups linked to the nitrogen is a linear or branched alkyl group of C8 to C18 carbon atoms. EP-A-188 025 teaches to use as a thickening surfactant one of these thickening surfactants. No acidic compositions comprising as a thickening system, a zwitterionic surfactant, e.g. a sulfobetaine and/or a betaine surfactant, together with an anionic surfactant at a weight ratio of the zwitterionic surfactant to the anionic surfactant of at least 2:1 is disclosed.

Summary of the invention

The compositions according to the present invention are liquid acidic thickened compositions having a viscosity of at least 10 m Pa s, when measured with a Carri-med rheometer at 5 N/m² at 20°C and a pH below 4, said composition comprising a thickening system comprising a zwitterionic surfactant and an anionic surfactant at a weight ratio of said zwitterionic surfactant to said anionic surfactant of at least 2:1, and from 0.1% to 70% by weight of the total composition of an acid or a mixture thereof.

The present invention also encompasses a process of treating a hard-surface, wherein a liquid thickened composition according to the present invention, is applied in its neat or diluted form onto said surface, optionally left to act thereto for an effective period of time and then removed.

Detailed description of the inventionThe liquid acidic thickened compositions

The liquid thickened compositions according to the present invention are preferably aqueous compositions. Therefore, they comprise from 50% to 98% by weight of the total composition of water, preferably from 60% to 95% and more preferably from 70% to 90%. One of the achievements of the present invention is that the viscosity build up described hereinafter can be achieved with such a high amount of water, i.e., a small amount of actives.

The liquid thickened compositions of the present invention are acidic compositions. Accordingly, the compositions of the present invention are formulated at a pH below 4, preferably at a pH between 0 and 3, more preferably at a pH between 0.1 and 2.5, even more preferably between 0.1 and 2, and most preferably at a pH between 0.3 and 1.5.

The compositions according to the present invention are designed for removing limescale deposits. Thus, they comprise as a first essential ingredient an acid or a mixture thereof. Typically, the acids to be used herein may be any inorganic or organic acid well-known to those skilled in the art, or a mixture thereof. Suitable acids for use herein include maleic acid, citric acid, adipic acid, sulfamic acid, phosphoric acid, nitric acid, malic acid, sulfonic acid, sulphuric acid or their salts or mixtures thereof. Indeed, such acids can be used in their acidic form or in the form of their salts (mono-, di-, tri- salts) and in all their anhydrous and hydrated forms, or mixtures thereof. Such acids may typically be used in the form of their alkali metal salts (e.g. sodium salt, potassium salt, and then like) or their alkali hydrogen acid salts. Said compositions comprise from 0.1% to 70% by weight of the total composition of an acid or a mixture thereof.

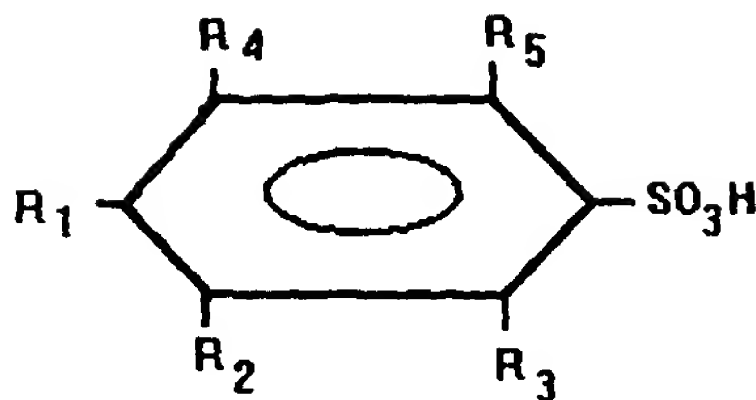
Preferred herein the compositions of the present invention comprise at least maleic acid. Accordingly, the compositions according to the present invention comprise from 0.1% to 45% by weight of the total composition of maleic acid, preferably from 1% to 25% and more preferably from 8% to 20%. This percentage is calculated on the basis of the molecular weight of the acid form, but maleic anhydride is equally convenient for use in the compositions according to the present invention. Indeed, maleic anhydride is generally cheaper and it is transformed into the acid form when incorporated in an aqueous medium. In one embodiment of the present invention maleic acid is used alone as the acid of the acidic compositions of the present invention.

In another embodiment of the present invention, a second acid is added on top of said maleic acid. Said second acid is desired to strengthen the limescale removal performance. Preferably the second acids to be used herein which are particularly efficient to remove limescale on many surfaces, have their first pKa not exceeding 5, more preferably not exceeding 3, and most preferably not exceeding 2. According to the present invention said acids can be organic or inorganic acids. Examples of inorganic acids are sulphonic acid derivatives, sulphamic acid (pKa=0.1), hydrochloric acid (pKa<0), nitric acid (pKa<0), phosphoric acid (pKa=2.1) and sulphuric acid (pKa=0.4). An example of organic acid is citric acid (pKa=3.06).

Particularly suitable to be used herein is sulphamic acid. Indeed, it has now been found that the addition of sulphamic acid on top of maleic acid in the compositions of the present invention improves the skin mildness of said compositions. Indeed, less skin irritation is perceived by the user when its skin comes into contact with these compositions as compared to the same compositions but without sulphamic acid.

Other suitable second acids are sulphonic acid derivatives including alkyl sulphonic acids and aryl sulphonic acids. Suitable alkyl sulphonic acids for use herein are C1-C6 linear or branched alkylsulphonic acids or mixtures thereof, such as methanesulphonic acid (pKa=1.9) commercially available for example from Aldrich, William Blythe & Co. Ltd. or Elf. Atochem.

Suitable aryl sulphonic acids for use herein are according to the formula:



wherein R₁, R₂, R₃, R₄ and R₅ are each H or SO₃H, or linear or branched C₁-C₄ alkyl chain; or mixtures thereof.

Preferred arylsulphonic acids to be used according to the present invention are those which comprise no alkyl chain or only one. Indeed, such arylsulphonic acids are particularly effective at removing limescale, which is not the case for their longer alkyl chain homologues. Also, such arylsulphonic acids are particularly safe to the surface treated therewith. Particularly suitable arylsulphonic acids for use herein are benzene sulphonic acid (pKa=0.7), toluene sulphonic acid and cumene sulphonic acid. Amongst these three, at equal weight %, we have found that the shorter the alkyl chain, down to no chain at all, the better the limescale removing performance.

Preferred acids having a first pKa not exceeding 5 to be used herein are sulphamic acid, sulphuric acid, aryl sulphonic acids, alkyl sulphonic acids, or mixtures thereof, more preferred are sulphamic acid, sulphuric acid, benzene sulphonic acid or mixtures thereof and highly preferred is sulphamic acid.

The compositions of the present invention comprise from 0.1% to 25% by weight of the total composition of a second acid which has a first pKa not exceeding 5, or mixtures thereof, preferably from 0.1% to 20%, more preferably from 0.1% to 10% and most preferably from 0.1% to 7%.

The compositions according to the present invention comprise as a second essential ingredient a surfactant system comprising a zwitterionic surfactant and an anionic surfactant at a weight ratio of the zwitterionic surfactant to the anionic surfactant of at least 2:1, preferably at least 3:1, more preferably from 10:1 to 3:1, even more preferably from 8:1 to 3:1 and most preferably from 6:1 to 3.5:1.

Indeed, it has unexpectedly been found that by combining a zwitterionic surfactant with an anionic surfactant as described herein at a weight ratio of the zwitterionic surfactant to the anionic surfactant of at least 2:1, in an acidic composition comprising an acid or a mixture thereof, a viscosity of at least 10 mPa s, is obtained, when measured with a Carri-med rheometer at 5 N/m² at 20°C, with a 4 cm diameter cone spindle, while exhibiting excellent physical and chemical stability.

The liquid acidic thickened compositions according to the present invention are chemically stable. By "chemically stable", it is meant herein that chemical parameters such as composition pH and/or acidity reserve do not change when the composition is stored in rapid aging test (RAT) at 50 °C for 6 days.

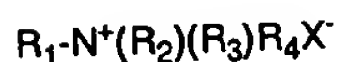
The liquid acidic thickened compositions according to the present invention are physically stable. By "physically stable", it is meant herein that neither phase separation nor viscosity changes occur when the composition is stored in rapid aging test (RAT) at 50 °C for 3 days or at 2 °C for 2 weeks.

The compositions of the present invention typically have a viscosity of from 10 mPa s to 1000 mPa s at 20°C, preferably from 10 mPa s to 400 mPa s, more preferably from 20 mPa s to 200 mPa s, and most preferably from 30 mPa s to 150 mPa s, when measured with a Carri-med rheometer CLS 100[®] by TA Instruments at 5 N/m² with a 4 cm diameter cone spindle.

Advantageously, the present invention allows to use low level of total thickening surfactants to achieve a given viscosity. The total level of thickening surfactants, i.e., of zwitterionic surfactants and anionic surfactants, to be used in a given acidic liquid composition depends on the thickness desired for said composition. Typically, the total level of thickening surfactants is lower than 20%, preferably between 0.5% and 8%, more preferably between 1% and 5%, and most preferably between 1% and 3.5%.

Suitable zwitterionic surfactants to be used herein contain at least one anionic and one cationic group in the molecule. Depending on the pH and in relation to their isoelectric area, they behave more cationically or more anionically, but usually exhibit both anionic and cationic type properties simultaneously over a wide pH range. The typical cationic group can be a secondary or tertiary ammonium group (so called "weak nitrogen zwitterionics") or a quaternary ammonium group (so called "betaines"), although other positively charged groups like phosphonium, imidazolium and sulfonium groups can be used. The main difference is that betaines carry a positive charge over the whole pH range, whereas weak nitrogen zwitterionics carry a positive charge only in acidic pH. The typical anionic hydrophilic groups are carboxylates and sulfonates, although other groups like sulfates, phosphonates, and the like can be used.

A generic formula for preferred zwitterionic surfactants to be used herein (i.e., betaine and/or sulfobetaine) is :



wherein R_1 is a hydrophobic group; R_2 is hydrogen, C_1 - C_6 alkyl, hydroxy alkyl or other substituted C_1 - C_6 alkyl group; R_3 is C_1 - C_6 alkyl, hydroxy alkyl or other substituted C_1 - C_6 alkyl group which can also be joined to R_2 to form ring structures with the N, or a C_1 - C_6 carboxylic acid group or a C_1 - C_6 sulfonate group; R_4 is a moiety joining the cationic nitrogen atom to the hydrophilic group and is typically an alkylene, hydroxy alkylene, or polyalkoxy group containing from 1 to 10 carbon atoms; and X is the hydrophilic group which is a carboxylate or sulfonate group, preferably a sulfonate group.

Preferred hydrophobic groups R_1 are aliphatic or aromatic, saturated or unsaturated, substituted or unsubstituted hydrocarbon chains that can contain linking groups such as amido groups, ester groups. More preferred R_1 is an alkyl group containing from 1 to 24 carbon atoms, preferably from 8 to 18, and more preferably from 10 to 16. These simple alkyl groups are preferred for cost and stability reasons. However, the hydrophobic group R_1 can also be an amido radical of the formula $R_a-C(O)-NR_b-(C(R_c)_2)_m$, wherein R_a is an aliphatic or aromatic, saturated or unsaturated, substituted or unsubstituted hydrocarbon chain containing from 8 up to 20 carbon atoms, preferably an alkyl group containing from 8 up to 20 carbon atoms, preferably up to 18, more preferably up to 16, R_b is either a hydrogen or a short chain alkyl or substituted alkyl containing from 1 to 4 carbon atoms, preferably a group selected from the group consisting of methyl, ethyl, propyl, hydroxy substituted ethyl or propyl and mixtures thereof, more preferably methyl or hydrogen, R_c is selected from the group consisting of hydrogen and hydroxy groups, and m is from 1 to 4, preferably from 2 to 3, more preferably 3, with no more than one hydroxy group in any $(C(R_c)_2)$ moiety.

Preferred R_2 is hydrogen, or an alkyl or substituted alkyl containing from 1 to 4 carbon atoms, preferably a group selected from the group consisting of methyl, ethyl, propyl, hydroxy substituted ethyl or propyl and mixtures thereof, more preferably methyl. Preferred R_3 is a C_1 - C_4 carboxylic acid group, a C_1 - C_4 sulfonate group, or an alkyl or substituted alkyl containing from 1 to 4 carbon atoms, preferably a group selected from the group consisting of methyl, ethyl, propyl, hydroxy substituted ethyl or propyl and mixtures thereof, more preferably methyl. Preferred R_4 is $(CH_2)_n$ wherein n is an integer from 1 to 10, preferably from 1 to 6, more preferably from 1 to 3.

Some common examples of betaine/sulphobetaine are described in U.S. Pat. Nos. 2,082,275, 2,702,279 and 2,255,082, incorporated herein by reference.

Examples of particularly suitable alkyldimethyl betaines include coconut-dimethyl betaine, lauryl dimethyl betaine, decyl dimethyl betaine, 2-(N-decyl-N, N-dimethyl-ammonia)acetate, 2-(N-coco N, N-dimethylammonio) acetate, myristyl dimethyl betaine, palmityl dimethyl betaine, cetyl dimethyl betaine, stearyl dimethyl betaine. For example Coconut dimethyl betaine is commercially available from Seppic under the trade name of Amonyl 265[®]. Lauryl betaine is commercially available from Albright & Wilson under the trade name Empigen BB/L[®].

A further example of betaine is Lauryl-immino-dipropionate commercially available from Rhone-Poulenc under the trade name Mirataine H2C-HA[®].

Particularly preferred zwitterionic surfactants to be used in the acidic compositions of the present invention are the sulfobetaine surfactants, as they deliver optimum limescale removal benefits, soap scum cleaning benefits and thickening benefits.

Examples of particularly suitable sulfobetaine surfactants include tallow bis(hydroxyethyl) sulphobetaines and cocoamido propyl hydroxy sulfobetaines which are commercially available from Rhone Poulenc and Witco, under the trade name of Mirataine CBS[®] and Rewoteric AM CAS 15[®] respectively.

Further examples of amidobetaines/sulfobetaines include cocoamidoethylbetaine, cocoamidopropyl betaine or C_{10} - C_{14} fatty acylamidopropylene(hydropropylene)sulfobetaine. For example C_{10} - C_{14} fatty acylamidopropylene(hydropropylene)sulfobetaine is commercially available from Sherex Company under the trade name "Varion CAS[®] sulfobetaine".

Typically the compositions according to the present invention comprise from 0.01% to 20% by weight of the total composition of a zwitterionic surfactant or mixtures thereof, preferably from 0.1% to 10% and most preferably from 0.5% to 5%.

Suitable anionic surfactants to be used herein as the cosurfactant include primary and secondary C_6 - C_{20} alkyl sulphonates, primary and secondary C_6 - C_{20} alkyl aryl sulphonates, C_6 - C_{20} alkyl sulphates, C_6 - C_{20} alkyl alkoxylated sulphonates, C_6 - C_{20} alkyl alkoxylated linear or branched diphenyl oxide disulphonates or other conventional anionic surfactants as mentioned herein after or mixtures thereof, preferably primary and secondary C_6 - C_{20} alkyl sulphonates, primary and secondary C_6 - C_{20} alkyl aryl sulphonates, C_6 - C_{20} alkyl sulphates, C_6 - C_{20} alkyl alkoxylated sulphonates, C_6 - C_{20} alkyl alkoxylated linear or branched diphenyl oxide disulphonates or mixtures thereof and more preferably primary and secondary C_6 - C_{20} alkyl sulphonates, primary and secondary C_6 - C_{20} alkyl aryl sulphonates or a mixture thereof.

Suitable alkyl sulphonates to be used herein include water-soluble salts or acids of the formula RSO_3M wherein R is a C_6 - C_{20} linear or branched, saturated or unsaturated alkyl group, preferably a C_{12} - C_{18} alkyl group and more preferably a C_{14} - C_{16} alkyl group, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium), or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations

derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like).

Suitable alkyl aryl sulphonates to be used herein include water-soluble salts or acids of the formula RSO_3M wherein R is an aryl, preferably a benzyl, substituted by a $\text{C}_6\text{-C}_{20}$ linear or branched saturated or unsaturated alkyl group, preferably a $\text{C}_{12}\text{-C}_{18}$ alkyl group and more preferably a $\text{C}_{14}\text{-C}_{16}$ alkyl group, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium, calcium, magnesium etc) or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like).

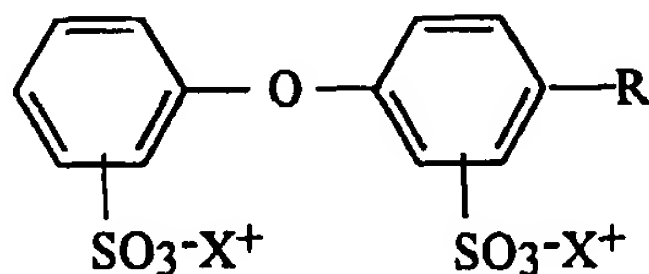
By "secondary $\text{C}_6\text{-C}_{20}$ alkyl or $\text{C}_6\text{-C}_{20}$ alkyl aryl sulphonates", it is meant herein that in the formula as defined above, the SO_3M or aryl- SO_3M group is linked to a carbon atom of the alkyl chain being placed between two other carbons of the said alkyl chain (secondary carbon atom).

An example of a $\text{C}_{14}\text{-C}_{16}$ alkyl sulphonate is Hostapur[®] SAS available from Hoechst. An example of commercially available alkyl aryl sulphonate is Lauryl aryl sulphonate from Su.Ma. Particularly preferred alkyl aryl sulphonates are alkyl benzene sulphonates commercially available under trade name Nansa[®] available from Albright&Wilson.

Suitable alkyl sulphate surfactants for use herein are according to the formula $\text{R}_1\text{SO}_4\text{M}$ wherein R_1 represents a hydrocarbon group selected from the group consisting of straight or branched alkyl radicals containing from 6 to 20 carbon atoms and alkyl phenyl radicals containing from 6 to 15 carbon atoms in the alkyl group. M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium, calcium, magnesium etc) or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like).

Suitable alkyl alkoxyated sulphate surfactants for use herein are according to the formula $\text{RO(A)}_m\text{SO}_3\text{M}$ wherein R is an unsubstituted $\text{C}_6\text{-C}_{20}$ alkyl or hydroxyalkyl group having a $\text{C}_6\text{-C}_{20}$ alkyl component, preferably a $\text{C}_{12}\text{-C}_{20}$ alkyl or hydroxyalkyl, more preferably $\text{C}_{12}\text{-C}_{18}$ alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium and quaternary ammonium cations, such as tetramethyl-ammonium, dimethyl piperdinium and cations derived from alkanolamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are $\text{C}_{12}\text{-C}_{18}$ alkyl polyethoxylate (1.0) sulfate, $\text{C}_{12}\text{-C}_{18}\text{E}(1.0)\text{M}$, $\text{C}_{12}\text{-C}_{18}$ alkyl polyethoxylate (2.25) sulfate, $\text{C}_{12}\text{-C}_{18}\text{E}(2.25)\text{M}$, $\text{C}_{12}\text{-C}_{18}$ alkyl polyethoxylate (3.0) sulfate $\text{C}_{12}\text{-C}_{18}\text{E}(3.0)$, and $\text{C}_{12}\text{-C}_{18}$ alkyl polyethoxylate (4.0) sulfate $\text{C}_{12}\text{-C}_{18}\text{E}(4.0)\text{M}$, wherein M is conveniently selected from sodium and potassium.

Suitable $\text{C}_6\text{-C}_{20}$ alkyl alkoxyated linear or branched diphenyl oxide disulphonate surfactants for use herein are according to the following formula:



wherein R is a $\text{C}_6\text{-C}_{20}$ linear or branched, saturated or unsaturated alkyl group, preferably a $\text{C}_{12}\text{-C}_{18}$ alkyl group and more preferably a $\text{C}_{14}\text{-C}_{16}$ alkyl group, and X^+ is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium, calcium, magnesium etc). Particularly suitable $\text{C}_6\text{-C}_{20}$ alkyl alkoxyated linear or branched diphenyl oxide disulphonate surfactants to be used herein are the C_{12} branched diphenyl oxide disulphonic acid and C_{16} linear diphenyl oxide disulphonate sodium salt respectively commercially available by DOW under the trade name Dowfax 2A1[®] and Dowfax 8390[®].

Other anionic surfactants useful herein include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, $\text{C}_8\text{-C}_{24}$ olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, $\text{C}_8\text{-C}_{24}$ alkylpolyglycol ethersulfates (containing up to 10 moles of ethylene oxide); alkyl ester sulfonates such as $\text{C}_{14}\text{-C}_{16}$ methyl ester sulfonates; acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated

C₁₂-C₁₈ monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C₆-C₁₄ diesters), acyl sarcosines, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), alkyl polyethoxy carboxylates such as those of the formula RO(CH₂CH₂O)_kCH₂COO-M⁺ wherein R is a C₈-C₂₂ alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23.

Typically the compositions of the present invention comprise from 0.001% to 10% by weight of the total composition of said anionic surfactant or mixtures thereof, preferably from 0.01% to 3%, more preferably from 0.1% to 1.5% and most preferably from 0.2% to 1%.

The self thickened surfactant system according to the present invention allows to lower the surface tension and to improve the wettability of the surfaces being cleaned with the liquid acidic compositions of the present invention. The presence of said surfactant system in the liquid acidic compositions of the present invention helps to solubilize the soils.

It has now been found that the addition, in an acidic liquid composition, of the surfactant system according to the present invention, i.e., a zwitterionic surfactant, as the primary surfactant, and a small amount of an anionic surfactant, as the co-surfactant, provides improved greasy soap scum cleaning performance as well as improved limescale removal performance, as compared to the greasy soap scum cleaning performance and limescale removal performance obtained with the same composition but with another surfactant system like for instance combination of nonionic surfactants, e.g. alcohol ethoxylate surfactants, instead of said surfactant system, this even at significantly lower total surfactant level.

More particularly, it has now unexpectedly been found that the zwitterionic surfactants as described herein, especially the sulfobetaine surfactants, act as lime soap dispersing agent. In presence of soap molecules (anionic surfactants) Ca cations coming from tap water are complexed by soap itself leading to formation of "soap scum" (also called "lime soap", i.e., insoluble organic calcium salts such as calcium stearate or calcium oleate) which precipitates. A lime soap dispersing agent is a compound that allows, thanks to its large head group, the formation of mixed micelles with soap molecules, thus avoiding formation and then precipitation of insoluble organic calcium salts.

In other words, it has been found that the addition of a zwitterionic surfactant, as defined herein, preferably sulfobetaine surfactant, in a liquid acidic composition reduces or even prevents deposition of soap scum on a hard-surface after the surface has been first treated with said composition, thereby ensuring long lasting soap scum cleaning benefit.

Optional ingredients:

The compositions according to the present invention may further comprise a variety of other ingredients including other surfactants, colorants, bactericides, polymers, dyes, chelants, pigments, solvents, stabilizers, perfumes, corrosion inhibitors and the like.

Polymers

In one embodiment of the present invention the compositions herein exhibit the desired viscosity due to the presence of the surfactant system described hereinbefore without the presence of a polymer. In another embodiment of the present invention where higher viscosity is desired, the compositions of the present invention may further comprise a charged polymer (i.e., a polymer which has either a positive or a negative charge when incorporated in the acidic compositions of the present invention). The addition of the polymer contributes to the formation of high micelle packing by the surfactant system that results in viscosity build up in the acidic compositions herein. Indeed, the addition of charged polymer exposing a charged backbone, in the acidic compositions of the present invention further enhances the surfactant system ability to form very tightly packed micelles and thus to increase the viscosity of the compositions.

Suitable polymers to be used herein including polycarboxylate polymers, sulphonated polystyrene polymers, vinylpyrrolidone homopolymer or copolymers, polyalkoxyethylene glycols, polysaccharide polymers or a mixture thereof.

Suitable polycarboxylate polymers for use herein are polymers comprising monomeric units selected from the group consisting of unsaturated carboxylic acids such as acrylic acid, polycarboxylic acids, sulphonic acids, phosphonic acids and mixtures thereof. Copolymerisation of the above monomeric units among them or with other co-monomers such as maleic anhydride, ethylene or propylene are also suitable. When used, maleic anhydride will act as a source of additional carboxylic groups, whilst ethylene and propylene will act as diluents.

The molecular weight per carboxylate group of monomers containing a carboxylate group typically varies from 20 to 200, preferably from 40 to 150, more preferably from 50 to 125. Preferred polymers for use herein have a total molecular weight of from 2,000 to 4,500,000, preferably from 10,000 to 4,000,000. Most preferred polymers for use herein contain from 0.5% to 4% by weight of a cross-linking agent, wherein the cross-linking agent tends to interconnect linear

strands of the polymers to form the resulting cross-linked products. Suitable cross-linking agents include the polyalkenyl polyethers.

Preferred polycarboxylate polymers for use herein are the polyacrylate polymers. Typically acrylic/maleic-based copolymers may be used as a preferred polyacrylate polymer. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 1,000,000, more preferably from about 5,000 to 100,000, most preferably from about 10,000 to 80,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982. Particularly preferred is a copolymer of maleic / acrylic acid with an average molecular weight of about 70,000. Such copolymers are commercially available from BASF under the trade name Sokalan CP5®.

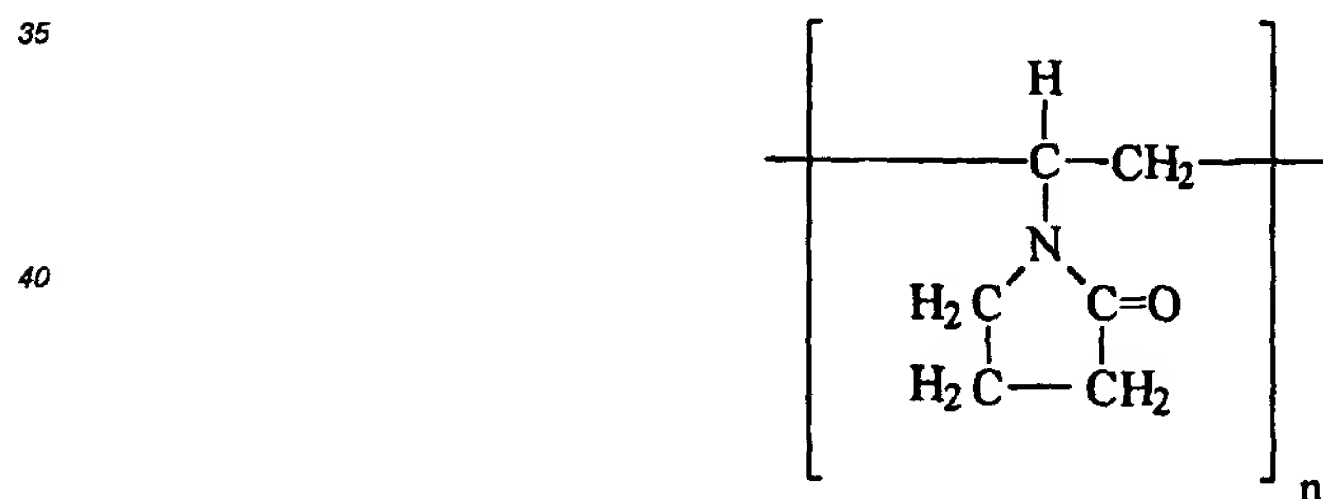
Other preferred polyacrylate polymers are the copolymer of acrylic acid and alkyl (C₅-C₁₀) acrylate, commercially available under the tradename Carbopol® 1623, Carbopol® 695 from BF Goodrich. Commercially available polymers of the polyacrylate type further include those sold under the trade names Carbopol®, Acrysol® ICS-1, Polygel®, and Sokalan®.

Two different types of sulfonated polystyrene polymers are useful herein. The first type is a sulfonated homopolymer of styrene. The second type is a sulfonated interpolymers of styrene with an ethylenically unsaturated comonomer. The useful compounds herein include the partially or fully neutralized salts of either the sulfonated polystyrene or the sulfonated styrene interpolymers, i.e. the soluble salts of these polymers, wherein the sulfonic acid groups are partially or fully neutralized.

Suitable ethylenically unsaturated comonomer units which can be copolymerized with styrene to make the interpolymers suitable for sulfation include acrylic and methacrylic esters of aliphatic alcohols such as methyl, ethyl, butyl and 2-ethyl hexyl alcohols, acrylic acid, acrylonitrile, methacrylonitrile, dibutyl maleate, vinylidene chloride and the like. Particularly preferred ethylenically unsaturated monomers for use herein include ethylene, propylene, styrene, vinyl naphthalene, acrylic acid and maleic anhydride.

Sulphonated styrene homopolymers suitable for use herein are commercially available under the trade name Versaflex® from National Starch. Most suitable polymers and copolymers for use herein will be water soluble, and the molecular weight for these polymers is preferably between 5000 and 10,000,000, most preferably between 50,000 and 1,000,000.

Suitable vinylpyrrolidone homopolymers to be used herein are homopolymers of N-vinylpyrrolidone having the following repeating monomer:



wherein n (degree of polymerisation) is an integer of from 10 to 1,000,000, preferably from 20 to 100,000, and more preferably from 20 to 10,000.

Accordingly, suitable vinylpyrrolidone homopolymers ("PVP") for use herein have an average molecular weight of from 1,000 to 100,000,000, preferably from 2,000 to 10,000,000, more preferably from 5,000 to 1,000,000, and most preferably from 50,000 to 500,000.

Suitable vinylpyrrolidone homopolymers are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15® (viscosity molecular weight of 10,000), PVP K-30® (average molecular weight of 40,000), PVP K-60® (average molecular weight of 160,000), and PVP K-90® (average molecular weight of 360,000). Other suitable vinylpyrrolidone homopolymers which are commercially available from BASF Cooperation include Sokalan HP 165® and Sokalan HP 12®; vinylpyrrolidone homopolymers known to persons skilled in the detergent field (see for example EP-A-262,897 and EP-A-256,696).

Suitable copolymers of vinylpyrrolidone for use herein include copolymers of N-vinylpyrrolidone and alkylenically unsaturated monomers or mixtures thereof.

The alkylenically unsaturated monomers of the copolymers herein include unsaturated dicarboxylic acids such as maleic acid, chloromaleic acid, fumaric acid, itaconic acid, citraconic acid, phenylmaleic acid, aconitic acid, acrylic acid, N-vinylimidazole and vinyl acetate. Any of the anhydrides of the unsaturated acids may be employed, for example acrylate, methacrylate. Aromatic monomers like styrene, sulphonated styrene, alpha-methyl styrene, vinyl toluene, t-butyl styrene and similar well known monomers may be used.

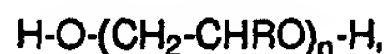
The molecular weight of the copolymer of vinylpyrrolidone is not especially critical so long as the copolymer is water-soluble, has some surface activity and is adsorbed to the hard-surface from the liquid composition or solution (i.e. under dilute usage conditions) comprising it in such a manner as to increase the hydrophilicity of the surface. However, the preferred copolymers of N-vinylpyrrolidone and alkylenically unsaturated monomers or mixtures thereof, have a molecular weight of between 1,000 and 1,000,000, preferably between 10,000 and 500,000 and more preferably between 10,000 and 200,000.

For example particularly suitable N-vinylimidazole N-vinylpyrrolidone polymers for use herein have an average molecular weight range from 5,000-1,000,000, preferably from 5,000 to 500,000, and more preferably from 10,000 to 200,000. The average molecular weight range was determined by light scattering as described in Barth H.G. and Mays J.W. Chemical Analysis Vol 113, "Modern Methods of Polymer Characterization".

Such copolymers of N-vinylpyrrolidone and alkylenically unsaturated monomers like PVP/vinyl acetate copolymers are commercially available under the trade name Luviskol® series from BASF.

The copolymers of vinylpyrrolidone for use in the compositions of the present invention also include quaternized or unquaternized vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymers. The preferred quaternized or unquaternized vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymers for use herein have a molecular weight of between 1,000 and 1,000,000, preferably between 10,000 and 500,000 and more preferably between 10,000 and 100,000. Such vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymers are commercially available under the name copolymer 845®, Gafquat 734®, or Gafquat 755® from ISP Corporation, New York, NY and Montreal, Canada or from BASF under the tradename Luviquat®.

Suitable polyalkoxyethylene glycols to be used herein have the following formula:



wherein R is hydrogen or a linear or branched hydrocarbon chain having from 1 to 30 carbon atoms, preferably R is hydrogen, or a linear or branched alkyl group, alkenyl group or aryl group having from 1 to 30 carbon atoms, more preferably from 1 to 16, even more preferably from 1 to 8, and most preferably R₂ is methyl, or hydrogen. Preferably n is an integer from 5 to 1000, more preferably from 10 to 100, even more preferably from 20 to 60 and most preferably from 30 to 50.

The preferred polyalkoxyethylene glycols to be used according to the present invention have a molecular weight of at least 200, more preferably from 400 to 5000 and most preferably from 800 to 3000.

Preferred polyalkoxyethylene glycols are polyethylene glycols like polyethylene glycol (MW 2000).

Suitable polysaccharide polymers for use herein include substituted cellulose materials like carboxymethylcellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxymethyl cellulose, succinoglycan and naturally occurring polysaccharide polymers like xanthan gum, guar gum, locust bean gum, tragacanth gum or derivatives thereof, or mixtures thereof. Particularly preferred polysaccharide polymers to be used herein are xanthan gum and derivatives thereof. Xanthan gum and derivatives thereof may be commercially available for instance from Kelco under the trade name Keltrol RD®, Kelzan S® or Kelzan T®.

Preferred acid-stable polymers to be used herein are the sulphonated polystyrene polymers and/or the vinylpyrrolidone homopolymers.

The compositions according to the present invention may comprise up to 3% by weight of the total composition of a polymer or mixture thereof preferably up to 1%, more preferably from 0.001% to 1% and most preferably from 0.01% to 0.5%.

Surfactants

The compositions according to the present invention may further comprise other surfactants apart the surfactant system described hereinbefore. The compositions according to the present invention may comprise up to 30% by weight of the total composition of said other surfactant or mixtures thereof on top of the surfactant system of the present invention, more preferably from 0.05% to 10%, more preferably from 0.1% to 8%, and most preferably from 0.1% to 3%. All types of surfactants may be used in the present invention including nonionic, anionic, cationic or amphoteric surfactants. It is also possible to use mixtures of such surfactants without departing from the spirit of the present invention.

Suitable nonionic surfactants to be used herein are alkoxyated alcohol nonionic surfactants which can be readily made by condensation processes which are well-known in the art. However, a great variety of such alkoxyated alcohols, especially ethoxylated and/or propoxylated alcohols is also conveniently commercially available. Surfactants catalogs are available which list a number of surfactants, including nonionics.

5 Accordingly, preferred alkoxyated alcohols for use herein are nonionic surfactants according to the formula $RO(E)_e(P)_pH$ where R is a hydrocarbon chain of from 2 to 24 carbon atoms, E is ethylene oxide and P is propylene oxide, and e and p which represent the average degree of, respectively ethoxylation and propoxylation, are of from 0 to 24. The hydrophobic moiety of the nonionic compound can be a primary or secondary, straight or branched alcohol having from 8 to 24 carbon atoms. Preferred nonionic surfactants for use in the compositions according to the invention are
10 the condensation products of ethylene oxide with alcohols having a straight alkyl chain, having from 6 to 22 carbon atoms, wherein the degree of ethoxylation is from 1 to 15, preferably from 5 to 12. Such suitable nonionic surfactants are commercially available from Shell, for instance, under the trade name Dobanol® or from Shell under the trade name Lutensol®. These nonionics are preferred because they have been found to allow the formulation of a stable product without requiring the addition of stabilisers or hydrotopes.

15 Suitable amine oxides to be used herein are according to the following formula $R_1R_2R_3NO$ wherein each of R1, R2 and R3 is independently a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group containing from 1 to 30 carbon atoms, and preferably from 1 to 20 carbon atoms. Particularly preferred amine oxides to be used according to the present invention are amine oxides having the following formula $R_1R_2R_3NO$ wherein R1 is a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group containing from 1 to 30 carbon
20 atoms, preferably from 8 to 20 carbon atoms, more preferably from 6 to 16, most preferably from 8 to 14, and wherein R2 and R3 are independently substituted or unsubstituted, linear or branched alkyl groups of from 1 to 4 carbon atoms, preferably from 1 to 3 carbon atoms, and more preferably are methyl groups, or mixtures thereof.

Suitable amine oxides for use herein are for instance coconut dimethyl amine oxides, C12-C16 dimethyl amine oxides. Said amine oxides may be commercially available from Hoechst, Stephan, AKZO (under the trade name Aromox®) or FINA (under the trade name Radiamox®).
25

Suitable amines to be used herein are according to the following formula $RR'R''N$ wherein R is a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group containing from 1 to 30 carbon atoms, and preferably from 1 to 20 carbon atoms and wherein R' and R'' are independently saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl groups containing from 1 to 30 carbon atoms or hydrogen. Particularly preferred
30 amines to be used according to the present invention are amines having the following formula $RR'R''N$ wherein R is a saturated or unsaturated, linear or branched alkyl group containing from 1 to 30 carbon atoms, preferably from 8 to 20 carbon atoms, more preferably from 6 to 16, most preferably from 8 to 14 and wherein R' and R'' are independently substituted or unsubstituted, linear or branched alkyl groups containing from 1 to 4 carbon atoms, preferably from 1 to 3 carbon atoms, and more preferably are methyl groups, or mixtures thereof.

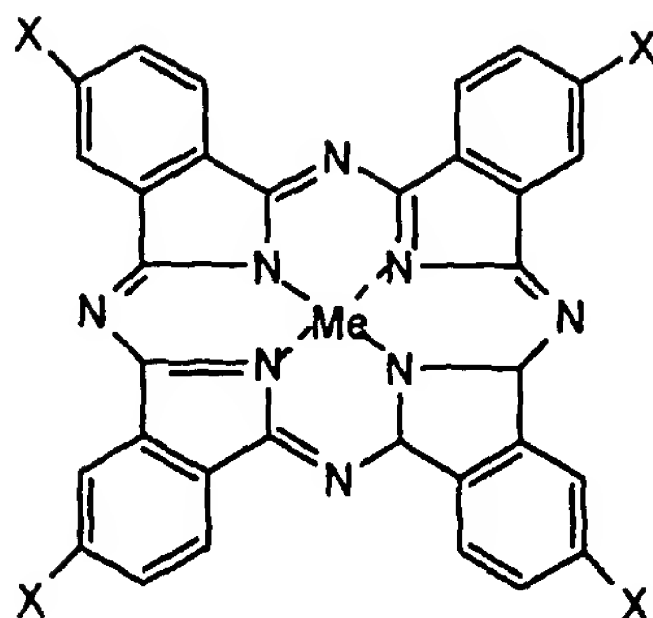
35 Suitable amines for use herein are for instance C12 dimethyl amine, coconut dimethyl amine, C12-C16 dimethyl amine. Said amines may be commercially available from Hoechst under the trade name Genamin®, AKZO under the trade name Aromox® or Fina under the trade name Radiamox®.

Suitable cationic surfactants to be used herein include derivatives of quaternary ammonium, phosphonium, imidazolium and sulfonium compounds. Preferred cationic surfactants for use herein are according to the formula
40 $R_1R_2R_3R_4N^+X^-$, wherein X is a counteranion, R₁ is a C₈-C₂₀ hydrocarbon chain and R₂, R₃ and R₄ are independently selected from H or C₁-C₄ hydrocarbon chains. In a preferred embodiment of the present invention, R₁ is a C₁₀-C₁₈ hydrocarbon chain, most preferably C₁₂, C₁₄, or C₁₆, and R₂, R₃ and R₄ are all three methyl, and X can be hydroxyl, methylsulphate or halogen, preferably bromide or chloride, most preferably bromide. Examples of cationic surfactants are lauryl trimethyl ammonium bromide, stearyl trimethyl ammonium bromide (STAB), cetyl trimethyl ammonium bromide (CTAB) and myristyl trimethyl ammonium bromide (MTAB). Highly preferred herein are lauryl trimethyl ammonium
45 salts.

Dyes

50 The liquid compositions according to the present invention may be colored. Accordingly, they may comprise a dye or a mixture thereof. Suitable dyes to be used herein are acid-stable dyes. By "acid-stable" it is meant herein a compound which is chemically and physically stable in the acidic environment of the compositions herein. Suitable dyes to be used herein include α or β metal phthalocyanines and/or trimethyl methane dyes.

The α or β metal phthalocyanine dyes suitable to be used in the compositions of the present invention are light-fast
55 organic pigments with four isoindole groups, $(C_6H_4)_4C_2N$, linked by four nitrogen atoms to form a conjugated chain. Their general structure is the following:



where the substituent X may be one of the following groups : H, Cl, HSO₃, COO-M⁺, Br, NO₂, OCH₃ or a C₁ to C₁₀ alkyl group and where Me is copper, chromium, vanadium, magnesium, nickel, platinum, aluminum, cobalt, lead, barium or zinc. Preferred α or β metal phthalocyanine dyes to be used herein are α or β copper phthalocyanine dyes.

Examples of such α copper phthalocyanine dyes to be used herein are copper phthalocyanine (X = H, blue colour) commercially available under the name *UNISPERSE Blue B-E*[®] from Ciba-Geigy, or *Cosmenyl blue A2R*[®] from Hoechst, or *Pigmosol blue 6900*[®] from BASF, or chlorinated copper phthalocyanine (X = Cl, green colour) commercially available under the name *Pigmosol Green 8730*[®] from BASF.

Examples of trimethyl methane dyes are commercially available from Hoescht under the name *Vitasyn*[®] or from BASF under the name *Acid Blue*[®].

These dyes and especially the α or β metal phthalocyanine dyes contribute to the benefit of the present invention, e.g., the ease of rinse perceived by the consumer when a hard-surface is treated with the compositions according to the present invention. Accordingly, the compositions of the present invention may comprise up to 0.2% by weight of the total composition of a dye or a mixture thereof, preferably from 0.001% to 0.015% and more preferably from 0.001% to 0.012%.

Packaging form of the liquid acidic thickened compositions:

The liquid acidic thickened compositions of the present invention may be packaged in a variety of suitable detergent packaging known to those skilled in the art.

Another advantage of the present invention is that the acidic liquid compositions of the present invention comprising an acid and the self-thickening surfactant system herein may be easily dispensed onto the surface to be treated via a spray-type dispenser such as for instance a trigger-sprayer. Accordingly, the present invention also encompasses liquid compositions of the invention packaged in a spray dispenser, preferably in a trigger spray dispenser or in a pump spray dispenser.

Suitable spray-type dispensers to be used according to the present invention include manually operated foam trigger-type dispensers sold for example by Specialty Packaging Products, Inc. or Continental Sprayers, Inc. These types of dispensers are disclosed, for instance, in US-4,701,311 to Dunning et al. and US-4,646,973 and US-4,538,745 both to Focarracci. Particularly preferred to be used herein are spray-type dispensers such as T 8500[®] or T 8900[®] commercially available from Continental Spray International or T 8100[®] commercially available from Canyon, Northern Ireland. In such a dispenser the liquid composition is divided in fine liquid droplets resulting in a spray that is directed onto the surface to be treated. Indeed, in such a spray-type dispenser the composition contained in the body of said dispenser is directed through the spray-type dispenser head via energy communicated to a pumping mechanism by the user as said user activates said pumping mechanism. More particularly, in said spray-type dispenser head the composition is forced against an obstacle, e.g. a grid or a cone or the like, thereby providing shocks to help atomise the liquid composition, i.e. to help the formation of liquid droplets.

A further advantage of the present invention is that the acidic liquid compositions of the present invention may be applied uniformly to a relatively large area of a surface to be treated via a spray-type dispenser, thereby ensuring improved limescale removal performance and improved greasy soap scum cleaning performance.

Process for manufacturing the liquid acidic thickened compositions:

The compositions according to the present invention may be manufactured by adding the different ingredients in

any order. However, the desired initial viscosity of an aqueous composition of the present invention is obtained immediately, when following a preferred mixing order for the incorporation of the different ingredients in said composition.

Accordingly, the present invention further encompasses a process for manufacturing the liquid acidic thickened compositions of the present invention, wherein said process comprises the steps of first preparing a water acidic solution with the desired pH by mixing the acids with water and then adding the other ingredients in the following order:

1. the primary surfactant, i.e. the zwitterionic surfactant,
2. optionally a perfume (if any),
3. the co-surfactant, i.e. the anionic surfactant,
4. optionally a polymer (if any) and finally other minors ingredients (if any) like for example a dye.

Process of treating surfaces:

The compositions according to the present invention are particularly suitable for treating hard-surfaces soiled by limescale-containing stains. By "limescale-containing stains", it is meant herein any pure limescale stains, i.e., any stains composed essentially of mineral deposits as well as limescale-containing stains typically found, for example, in a kitchen or in a bathroom, i.e., stains which contain not only mineral deposits like calcium and/or magnesium carbonate but also soap scum (e.g., calcium stearate) and other grease. Actually, the compositions of the present invention exhibit excellent limescale removing performance when used to treat any types of surfaces soiled by limescale-containing stains comprising not only pure limescale deposits but also at least 10% by weight of the total stain of organic deposits like soap scum and grease, preferably more than 30%. Such surfaces can be found in bathrooms, kitchens, but also in appliances including large appliances such as automatic dish washers and/or washing machines.

Accordingly, the present invention encompasses a process of treating hard-surfaces soiled by limescale-containing stains wherein an aqueous acidic liquid composition according to the present invention is applied in its neat form or in diluted form, onto said surfaces, then left to act onto said surfaces and then removed by rinsing.

The expression "used in diluted form" herein includes dilution by the user. Typical dilution levels are of from 0.5% to 50% by weight of the composition.

The expression "treating" includes removing limescale deposits while being safe to the surfaces treated as well as cleaning greasy soap scum stains due to the presence of said surfactant system.

Limescale removal performance test method:

The limescale removal capacity of a composition according to the present invention may be evaluated by soaking a marble block (marble blocks are chemically speaking very similar to limescale, i.e. they are essentially made of calcium carbonate) into 20 g of this composition. The marble is weighed before and after the experiment, and the performance is expressed in grams of marble block dissolved over time. Alternatively, limescale removal performance can also be evaluated by detecting the release of CO₂.

Greasy soap scum cleaning performance test method:

In this test method enamel white tiles (typically 24 cm * 4 cm) are covered with typical greasy soap scum soils mainly based on calcium stearate and artificial body soils commercially available (e.g. 0.3 grams with a sprayer). The soiled tiles are then dried in an oven at a temperature of 140 °C for 30 minutes and then aged overnight at room temperature (around 15°C-20°C). Then the soiled tiles are treated with a Spontex® sponge impregnated with the liquid acidic composition of the present invention (e.g. 5 grams). The ability of the composition to remove greasy soap scum is measured through the number of strokes needed to perfectly clean the surface. The lower the number of strokes, the higher the greasy soap scum cleaning ability of the composition.

Test method to evaluate lime soap dispersing ability of a compound:

This test method can be carried out as described herein: 5 ml of sodium oleate (0.5g/100ml) is pipetted into a test tube and an arbitrary amount of lime soap dispersing agent (e.g. 5 ml of 0.25g/100ml solution) is added, followed by 10ml of hard water (60% calcium and 40% magnesium totalling 1g/l calculated as Ca CO₃ = 70° English hardness). The volume is then made up to 30ml with distilled water. The test tube is stoppered and inverted 20 times, and then allowed to stand for 30 seconds after which the condition of the lime soap particles is observed. The test is repeated to determine the minimum amount of lime soap dispersing agent (LSDA) in gram (A in the following equation) to prevent formation of a coagulated precipitate, i.e. the lime soap particles. The solution becomes translucent just before this end point. The measurement of lime soap dispersing ability is given by the following formula:

$$\% \text{ lime soap dispersing ability} = \frac{A \text{ (in grams)}}{0.025 \text{ (weight of sodium oleate)}} \times 100$$

The lower the % lime soap dispersing ability, the better the LSDA ability of said compound. This test method, also called "Borghetty and Bergman test" can be found in literature (JAOCS vol 27 pag. 88-90).

Examples

The present invention is further illustrated by the following examples. These compositions were made comprising the listed ingredients in the listed proportions (weight %).

Compositions

Ingredients: (% by weight)	I	II	III	IV	V	VI
Maleic acid	10	10	10	10	10	10
Sulphamic acid	2	2	2	2	2	2
Mirataine CBS® (*)	2.2	2.3	2.5	2.3	2.2	-
Rewoteric AM CAS 15® (*)	-	-	-	-	-	2.2
HLAS (**)	-	-	-	0.53	0.50	-
Na LAS (**)	-	-	-	-	-	0.53
Hostapur SAS® (***)	0.48	-	-	-	-	-
C12/C14 alkyl sulphate	-	0.76	-	-	-	-
Na dodecyl sulphate	-	-	0.80	-	-	-
Waters & Minors	up to 100					
Viscosity (mPas)(****)	100	110	80	140	90	45

(*) Mirataine CBS® and Rewoteric AM CAS® 15 are examples of cocoamidopropyl hydroxy sulphobetaine supplied respectively by Rhone-Poulenc and Witco.

(**) HLAS is Linear alkyl benzene sulphonate in acid form while Na LAS is its sodium salt.

(***) Hostapur SAS® is a secondary alkane sulphonate supplied by Hoechst

(****) Viscosity grows with time; therefore, those are the value measured just after product making, i.e., they are the lowest achievable viscosities with the above indicated compositions.

Ingredients: (% by weight)	VII	VIII	IX	X	XI	XII
Maleic acid	10	10	10	10	10	10
Sulphamic acid	2	2	2	2	2	2
Mirataine CBS® (*)	2.2	2.2	2.3	2.0	1.9	-
Rewoteric AM CAS 15® (*)	-	-	-	-	-	2.2
HLAS (**)	-	-	0.53	0.50	0.50	-
Na LAS	0.45	-	-	-	-	-
Hostapur SAS®	-	0.55	-	-	-	0.8
C12/C14 alkyl sulphate	-	-	-	-	-	-
Na dodecyl sulphate	-	-	-	-	-	-
Polyvinyl pyrrolidone	-	0.03	-	0.05	-	-
Polystyrene Sulphonate	-	-	0.05	-	0.05	0.05
Waters & Minors	up to 100					
Viscosity (mPas) (****)	80	70	150	50	40	45

(*) Mirataine CBS® and Rewoteric AM CAS® 15 are examples of cocoamidopropyl hydroxy sulphobetaine supplied respectively by Rhone-Poulenc and Witco.
(**) HLAS is Linear alkyl benzene sulphonate in acid form while Na LAS is its sodium salt.
(****) Viscosity grows with time; therefore, those are the value measured just after product making, i.e., they are the lowest achievable viscosities with the above indicated compositions.

Ingredients: (% by weight)	XIII	XIV	XV	XVI	XVII	XVIII
Maleic acid	12	14	8	14	10	8
Sulphamic acid	-	2	4	-	-	-
Citric acid	-	-	-	-	3	-
Benzenesulphonic acid	-	-	-	-	-	2
Mirataine CBS® (*)	2.2	2.3	2.5	2.3	2.2	-
Rewoteric AM CAS 15® (*)	-	-	-	-	-	2.2
HLAS (**)	-	-	-	0.53	0.50	-
Na LAS (**)	-	-	-	-	-	0.53
Hostapur SAS® (***)	0.48	-	-	-	-	-
C12/C14 alkyl sulphate	-	0.76	-	-	-	-
Na dodecyl sulphate	-	-	0.80	-	-	-
Polystyrene Sulphonate	-	-	-	0.05	-	-
Waters & Minors	up to 100					
Viscosity (mPas)(****)	100	110	80	140	90	45

(*) Mirataine CBS® and Rewoteric AM CAS® 15 are examples of cocoamidopropyl hydroxy sulphobetaine supplied respectively by Rhone-Poulenc and Witco.

(**) HLAS is Linear alkyl benzene sulphonate in acid form while Na LAS is its sodium salt.

(***) Hostapur SAS® is a secondary alkane sulphonate supplied by Hoechst

(****) Viscosity grows with time; therefore, those are the value measured just after product making, i.e., they are the lowest achievable viscosities with the above indicated compositions.

The initial viscosity of the above compositions were measured by a Carri-Med Rheometer CLS 100® by TA instruments at fixed shear stress of 5 N/m² at 20°C with a 4 cm diameter cone spindle. 50 N/m² as shear stress value is representative of a fluid flow occurring on an inclined surface when the product thickness on the surface is about 1 mm and the only external force is due to the gravity field.

All the above compositions according to the present invention are translucent, Newtonian compositions that provide significant benefits in limescale removal applications. Indeed, all the compositions of the above examples exhibit excellent limescale removal performance as well as outstanding greasy soap scum cleaning performance when used to clean limescale-containing stains found in a kitchen and in a bathroom, this both when used neat or in diluted form. These compositions also ensure long lasting soap scum cleaning to the surface having been treated therewith.

Claims

1. A liquid acidic thickened composition having a viscosity of at least 10 m Pa s, when measured with a Carri-med rheometer at 5 N/m² at 20°C with a 4 cm diameter cone spindle, and a pH below 4, said composition comprising a self-thickening system comprising a zwitterionic surfactant and an anionic surfactant at a weight ratio of said zwitterionic surfactant to said anionic surfactant of at least 2:1, and from 0.1% to 70% by weight of the total composition of an acid.
2. A composition according to claim 1 wherein said acid is an organic or inorganic acid or a mixture thereof.
3. A composition according to any of the preceding claims wherein said acid is maleic acid alone or together with a second acid which has its first pKa not exceeding 5, or mixtures thereof.
4. A composition according to claim 3 wherein said second acid is sulphamic acid, alkylsulfonic acid, arylsulfonic acid,

citric acid, nitric acid, sulphuric acid, phosphoric acid, hydrochloric acid or a mixture thereof and preferably sulphamic acid.

- 5 5. A composition according to claims 3 or 4 wherein said composition comprises from 0.1% to 45% by weight of the total composition of maleic acid, preferably from 1% to 25%, and more preferably from 8% to 20%, and optionally from 0.1% to 25% by weight of the total composition of said second acid, or mixtures thereof, preferably from 0.1% to 20%, and more preferably from 0.1% to 10%.

- 10 6. A composition according to any of the preceding claims wherein said zwitterionic surfactant is according to the formula:



15 wherein R_1 is an aliphatic or aromatic, saturated or unsaturated, substituted or unsubstituted hydrocarbon chain that can contain linking groups such as amido groups, ester groups, preferably an alkyl group containing from 1 to 24 carbon atoms, more preferably from 8 to 18, or an amido radical of the formula $R_a-C(O)-NR_b-(C(R_c)_2)_m$, wherein R_a is an aliphatic or aromatic, saturated or unsaturated, substituted or unsubstituted hydrocarbon chain containing from 8 up to 20 carbon atoms, preferably an alkyl group containing from 8 up to 18 carbon atoms, R_b is either a hydrogen a short chain alkyl or substituted alkyl containing from 1 to 4 carbon atoms, preferably a group selected from the group consisting of methyl, ethyl, propyl, hydroxy substituted ethyl or propyl and mixtures thereof, more preferably methyl or hydrogen, R_c is selected from the group consisting of hydrogen and hydroxy groups, and m is from 1 to 4, preferably from 2 to 3, more preferably 3, with no more than one hydroxy group in any $(C(R_c)_2)$ moiety;

25 R_2 is hydrogen, C_1 - C_6 alkyl, hydroxy alkyl or other substituted C_1 - C_6 alkyl group;

R_3 is C_1 - C_6 alkyl, hydroxy alkyl or other substituted C_1 - C_6 alkyl group which can also be joined to R_2 to form ring structures with the N, or a C_1 - C_6 carboxylic acid group or a C_1 - C_6 sulfonate group;

30 R_4 is a moiety joining the cationic nitrogen atom to the hydrophilic group and is typically an alkylene, hydroxy alkylene, or polyalkoxy group containing from 1 to 10 carbon atoms;

and X is the hydrophilic group which is a carboxylate or sulfonate group.

- 35 7. A composition according to any of the preceding claims wherein said anionic surfactant is a primary or secondary C_6 - C_{20} alkyl sulphonate, primary or secondary C_6 - C_{20} alkyl aryl sulphonate, C_6 - C_{20} alkyl sulphate, C_6 - C_{20} alkyl alkoxylated sulphate, C_6 - C_{20} alkyl linear or branched diphenyl oxide disulphonates or a mixture thereof, and preferably is a primary or secondary C_6 - C_{20} alkyl sulphonate, primary or secondary C_6 - C_{20} alkyl aryl sulphonate or a mixture thereof.

- 40 8. A composition according to any of the preceding claims wherein said composition comprises a total level of thickening surfactant lower than 20%, preferably between 0.5% and 8%, more preferably between 1% and 5%, and most preferably between 1% and 3.5%.

- 45 9. A composition according to any of the preceding claims wherein the weight ratio of said zwitterionic surfactant to said anionic surfactant is at least 3:1, preferably from 10:1 to 3:1 and more preferably from 6:1 to 3.5:1.

10. A composition according to any of the preceding claims wherein said composition has a viscosity from 10 m Pa s to 400 m Pa s, more preferably from 20 m Pa s to 200 m Pa s, and most preferably from 30 m Pa s to 150 m Pa s.

- 50 11. A composition according to any of the preceding claims wherein said composition has a pH below 3, preferably a pH of from 0.1 to 2.5 and more preferably of from 0.1 to 2.

- 55 12. A composition according to any of the preceding claims wherein said composition further comprises a charged polymer or a mixture thereof up to a level of 3%, preferably up to 1%, more preferably from 0.001% to 1% and most preferably from 0.01% to 0.5% and wherein said polymer preferably is a polycarboxylate polymer, a sulphonated polystyrene polymer, a vinylpyrrolidone homopolymer or copolymer, a polyalkoxyethylene glycol, a polysaccharide polymer or a mixture thereof.

13. A process of treating a hard-surface soiled by limescale-containing stains, wherein an acidic liquid composition according to any of the preceding claims is applied in its neat form or in diluted form, onto said surface, then left to act onto said surfaces, and then removed by rinsing.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 97 87 0057

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	DATABASE WPI Section Ch, Week 9125 Derwent Publications Ltd., London, GB; Class A97, AN 91-182435 XP002042786 & JP 03 111 494 A (LION CORP) , 13 May 1991 * abstract *	1,2,6,7	C11D1/94 C11D17/00
A	--- EP 0 601 990 A (PROCTER & GAMBLE) 15 June 1994 * claims *	1-3,8	
A	--- EP 0 342 786 A (CLOROX CO) 23 November 1989 * claim 1 *	1,6	
A	--- EP 0 518 401 A (PROCTER & GAMBLE) 16 December 1992 * claim 1; examples *	1-4	
A	--- EP 0 606 712 A (CLOROX CO) 20 July 1994 * claims; examples * -----	1,2,7,8,13	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C11D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 7 October 1997	Examiner Grittern, A
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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